

Approach to Recycle Sodium (Caustic) from Low Level Radioactive Stream Using NaSICON Technology

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Outline

- ❖ Opportunity
- ❖ Technology Description
- ❖ Development Status
- ❖ FY07 Testing Results
- ❖ Cost Analysis
- ❖ Preconceptual Design

Opportunity

- ❖ **Problem:** DOE site at Hanford has sodium contaminated sodium salts in 177 radioactive contaminated tanks. The site can use up to 39,000 MT of Na needed for WTP pretreatment



Hanford Site

- ❖ **Solution:** Ceramatec's NASICON patented technology can recycle sodium from contaminated low level radioactive waste.
- ❖ **Result:**
 - (1) Potential to reduce handling, processing, of waste and Time Schedule at DOE sites.
 - (2) Potential cost savings by lowering volume of waste.

Technology Description

- ◆ NaSICON electrochemical membrane technology separates sodium from LAW waste stream to reduce the quantity of LAW glass produced
- ◆ The process also regenerates the sodium in the form of “clean” sodium hydroxide for reused on site
- ◆ NaSICON ceramic membrane technology is used to allow direct sodium hydroxide generation up to 50 wt% and prevent migration of Cs and other radionuclides to the sodium hydroxide stream.
- ◆ Ceramic is also resistant to radiation damage

Introduction: NaSICON-Membranes

Definition

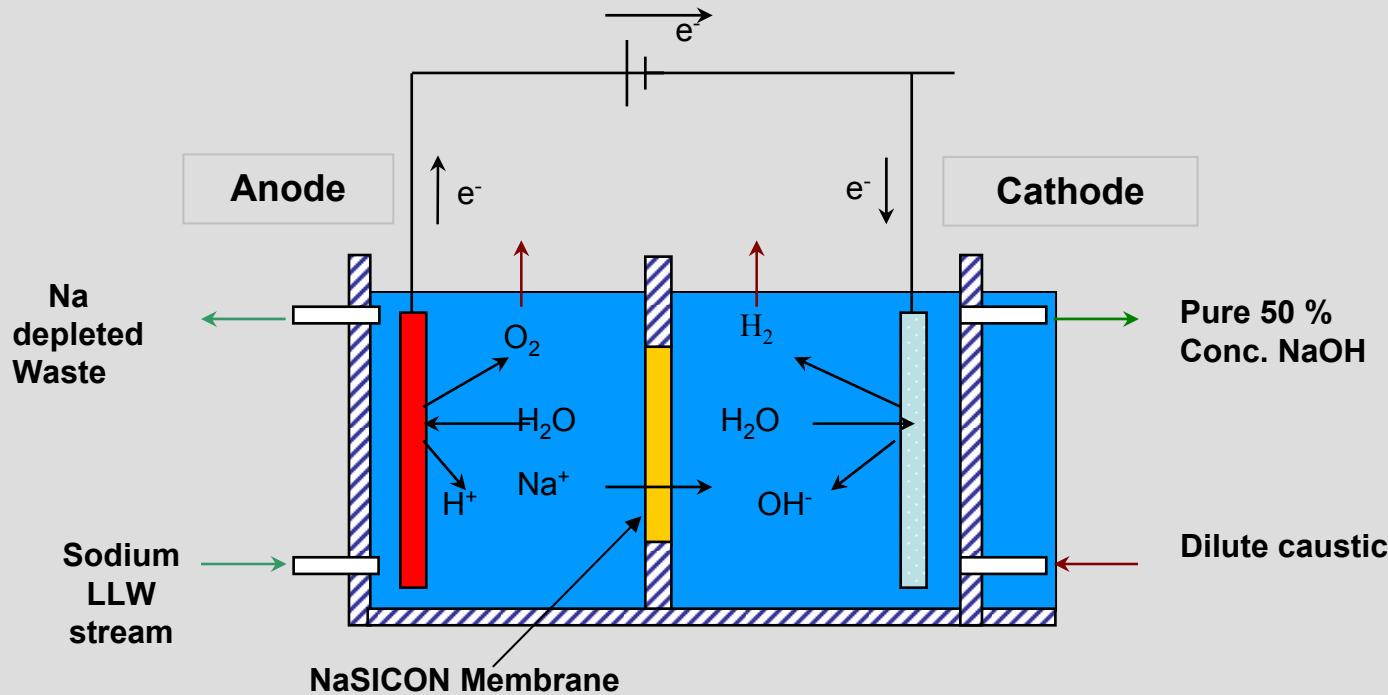
Na = Sodium

SI = Super Ionic

CON = Conductors

- Family of Sodium Phosphate Ceramics
- Originally Developed for Na-S Battery Applications
- Unlike polymer membranes does not foul in presence of solids or complex elements
- Sodium ionic conductivity is 13 ms/cm at 40°C
- Membranes are chemically stable to corrosive chemicals and operates in a wide pH range
- Selectively transports sodium ions over other ions present in salt streams

Principle of Operation: Electrolytic NaSICON Ceramic membrane cell



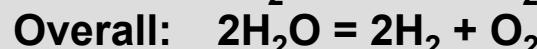
NaSICON Membrane

Na=Sodium

SI=Super Ionic

CON= Conductors

Electrode Reactions:



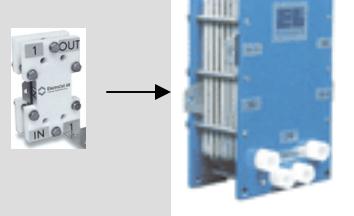
Why Ceramic Membranes

- ❖ Good radiation resistance
 - ❖ reduces maintenance costs
- ❖ Resistant to fouling
 - ❖ reduces maintenance costs
- ❖ High selectivity for sodium
 - ❖ good product purity
 - ❖ high current efficiency (> 95 %)
 - ❖ Radioactive stable (tested to 10^9 rad)
- ❖ Concentrated product (50 wt%) directly produced

DESIGN: Progression Plan of Electrolytic unit

Bench Scale Prototype

Concept-
Microflow Cell



3.29 g_{Na⁺}/day/scaffold

Laboratory-
MP Cell



Up to 39 g_{Na⁺}/day/scaffold

313 g_{Na⁺}/day/scaffold

Production full size

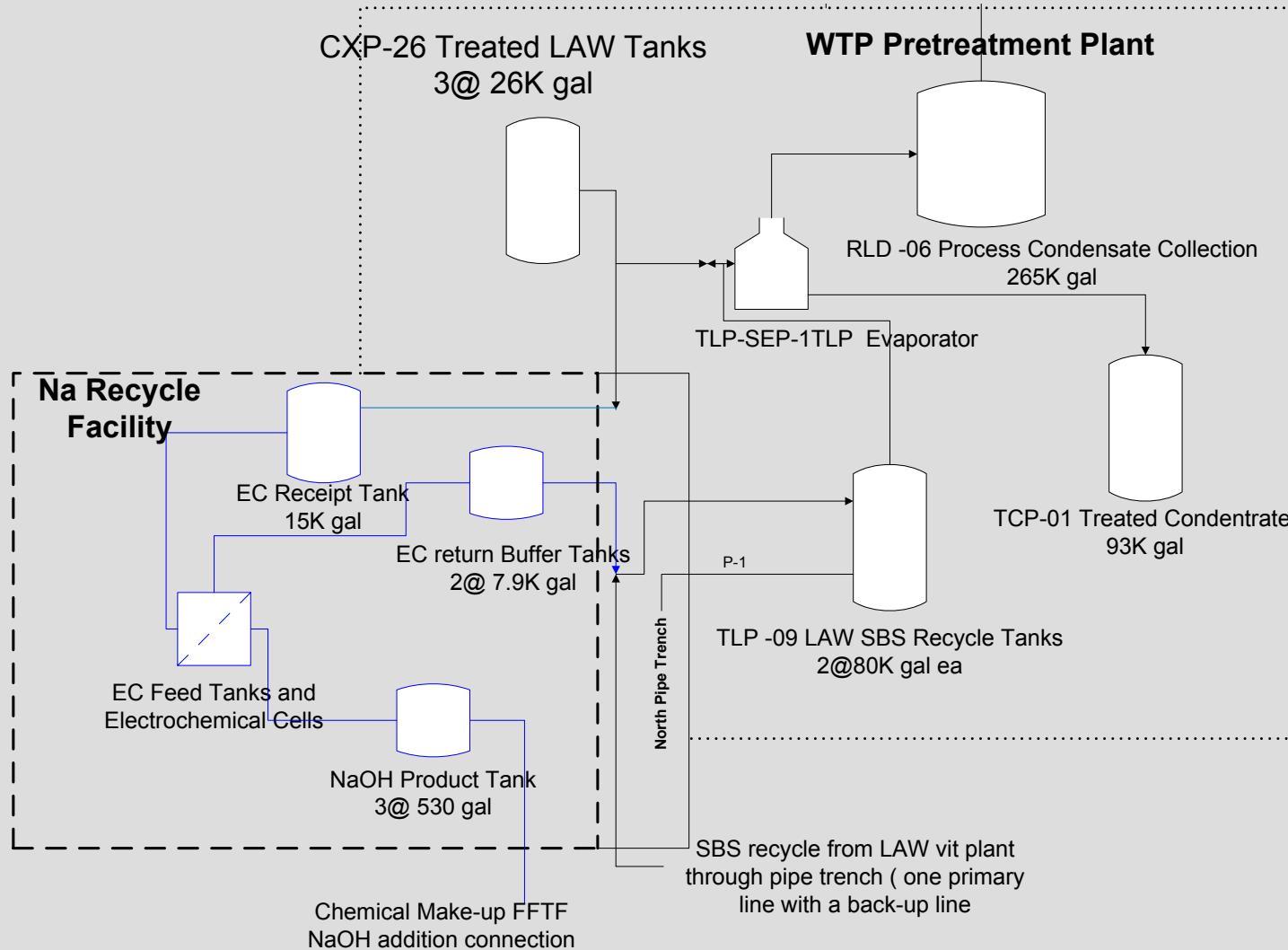


> 1.4 kg_{Na⁺}/day/scaffold

- Production rates based on 50 mA/cm²
- Device scales linearly
- Design and hydrodynamics established
- Retrofit and process engineering of ceramic scaffold

Commercial Cells-Figures are not to scale

WTP Process Integration



Testing with Simulant

- ◆ Lab scale tests being conducted over 3800 hrs of continues operation at Ceramatec Inc.
- ◆ NASICON membrane NASGY LANS Ceramics
- ◆ Testing performed at 50mA/cm²
 - ◆ Anolyte mixed waste simulant (AP104 based)
 - ◆ 50 wt % NaOH Catholyte

Electrolytic Prototype cell Set Up

Anolyte/Catholyte

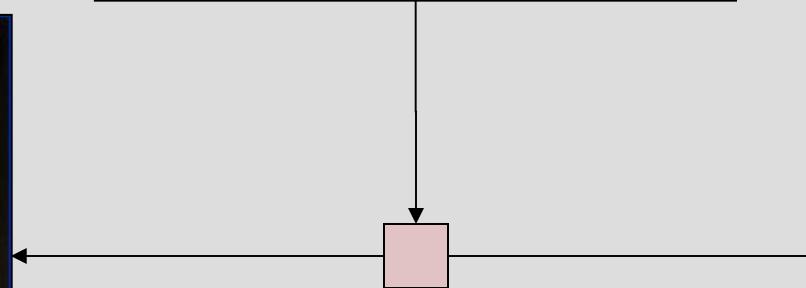
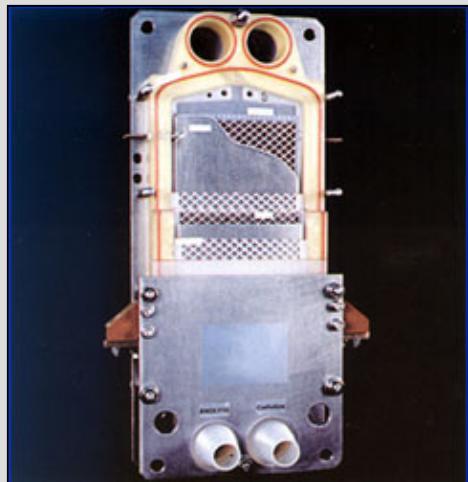
Feed: 2 gpm

Tank size: 25 Gallons

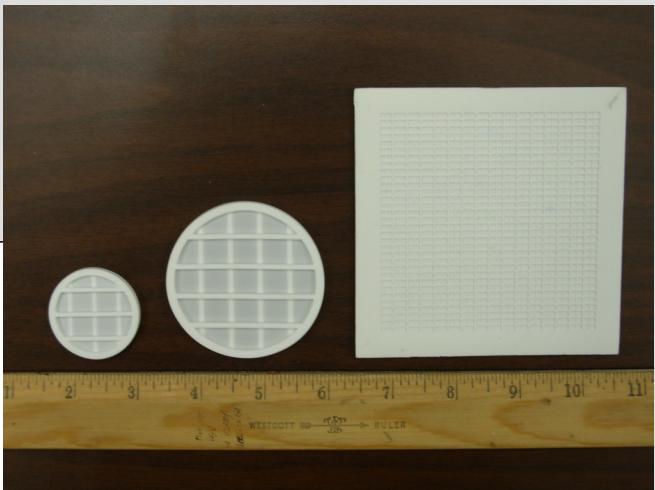
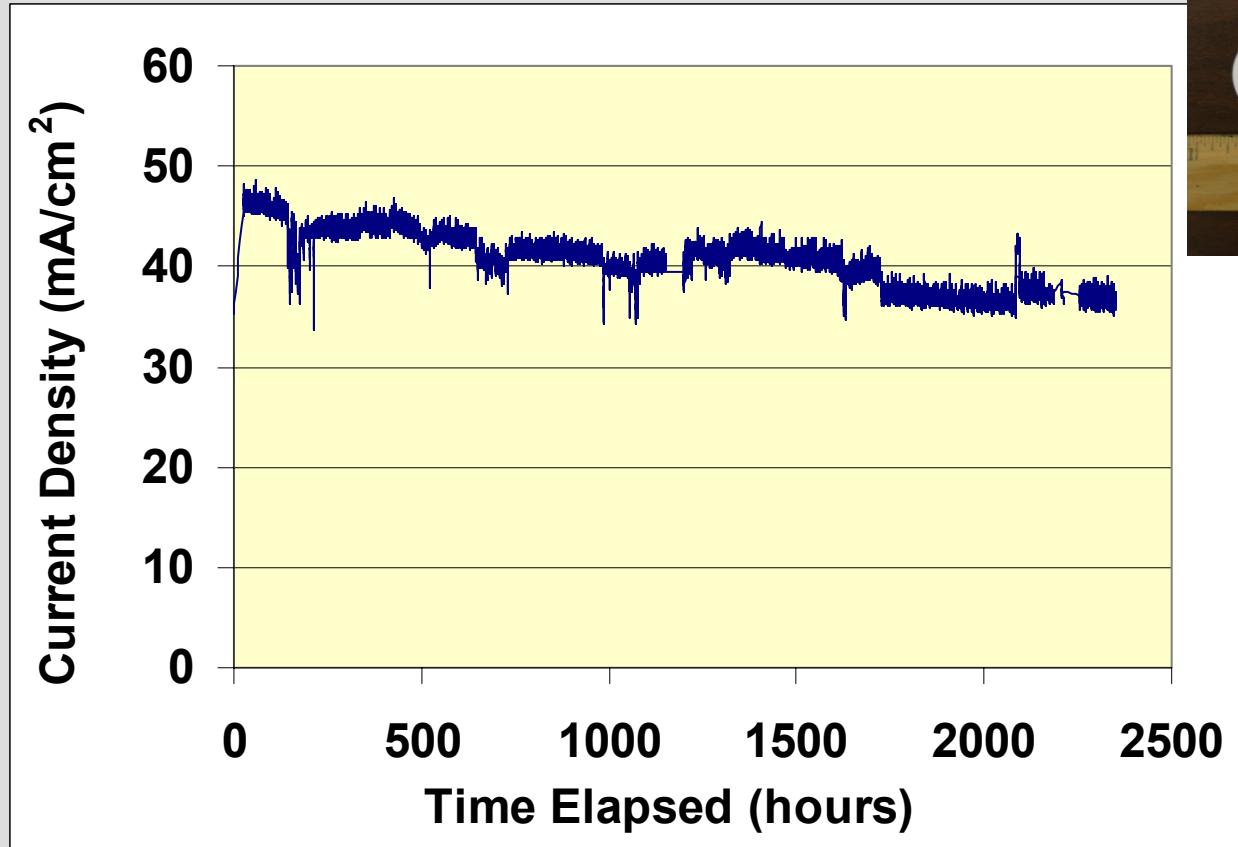
Laboratory Scale



Pilot Scale

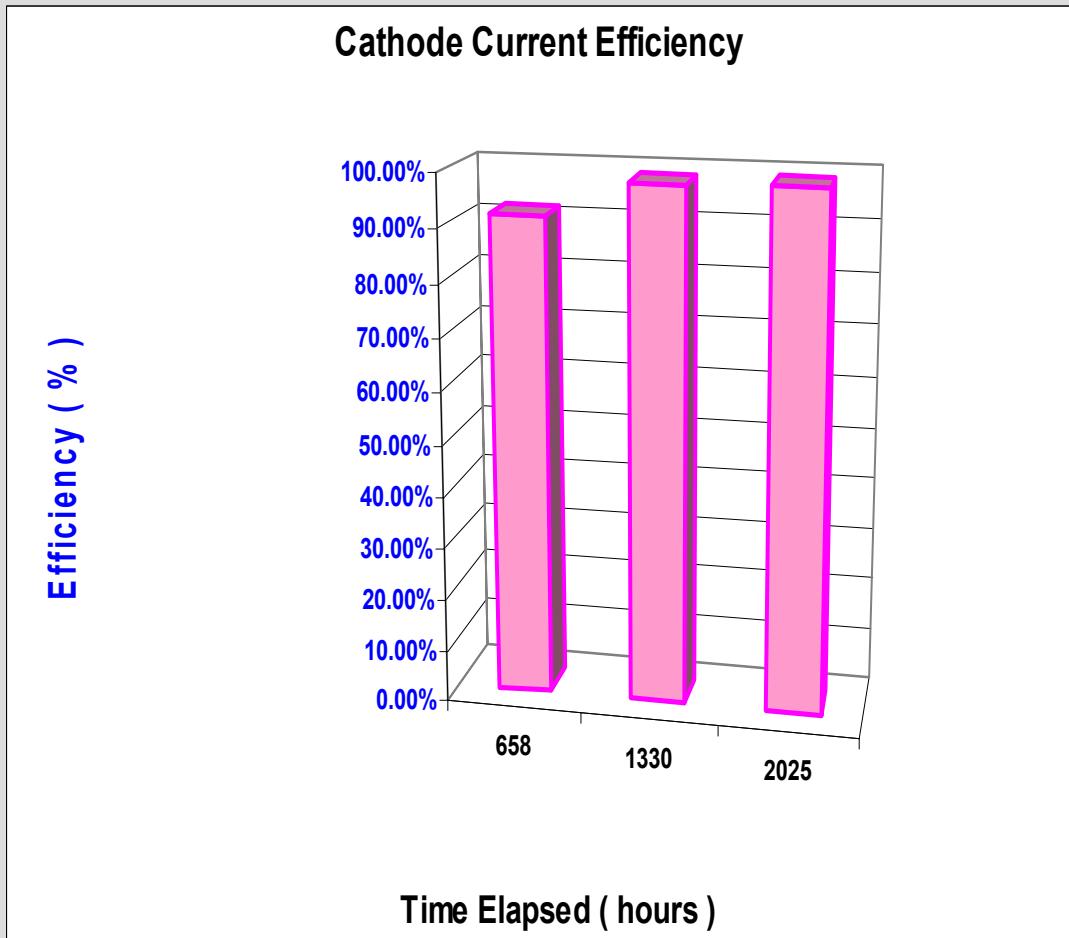


LANS Testing with 50% NaOH catholyte

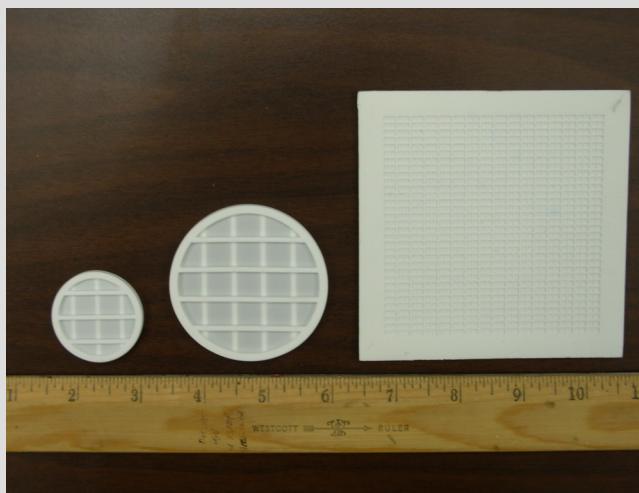
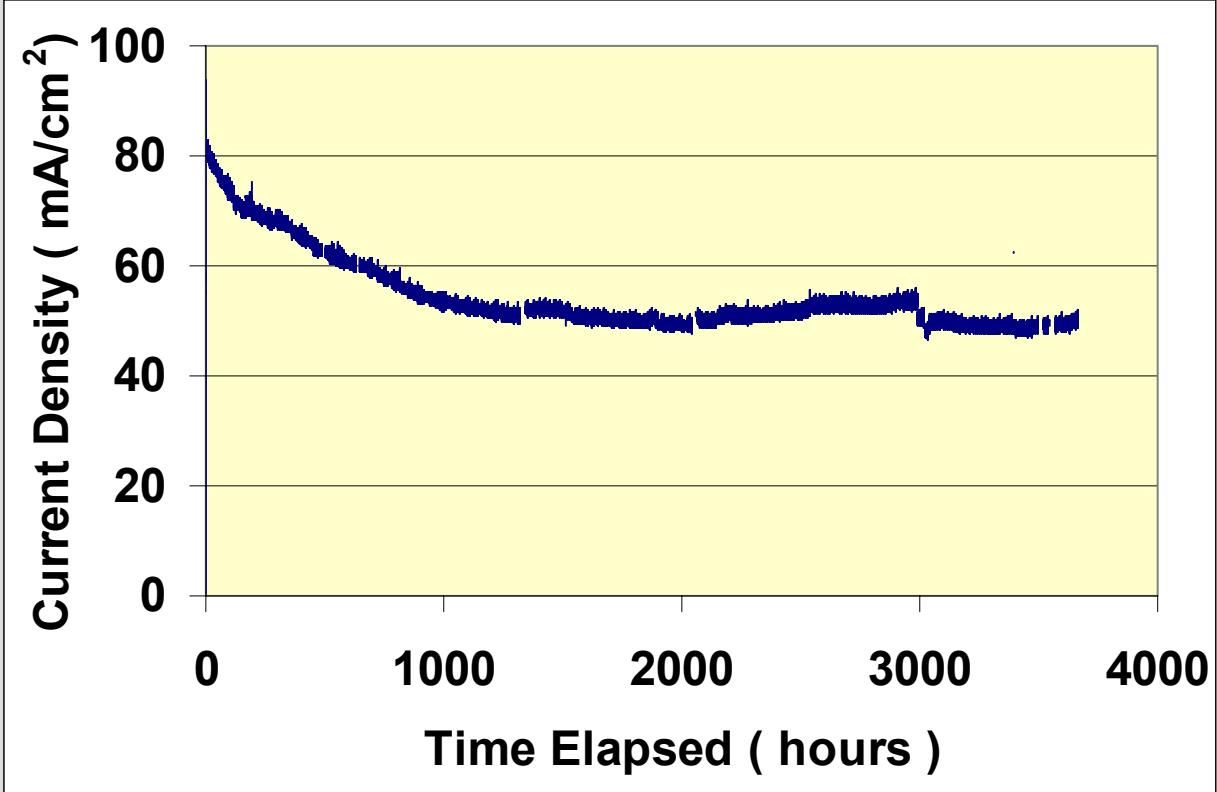


- Voltage limit: 2.6
- Temp.: 40°C
- Anode: Kovar
- Cathode: Ni
- Anolyte: AP104
- Catholyte: 47 to 50% NaOH
- Cell Configuration: MP Cell
- **Testing still in progress as of 10/8/07**

Testing with Simulants



LANS Testing with ICON Anode



- Voltage limit: 2.6
- Temp.: 40°C
- Anode: Kovar
- Cathode: Ni
- Anolyte: AP104
- Catholyte: 47 to 50% NaOH
- Cell Configuration: MP Cell
- Testing still in progress as of 10/8/07

Summary of LANS Testing

Cell Voltage	Average Current Density	Lifetime
3.0	75 mA/cm ²	3000 hrs
2.8	60 mA/cm ²	2500 hrs
2.6	50 mA/cm ²	3800 hrs and still going

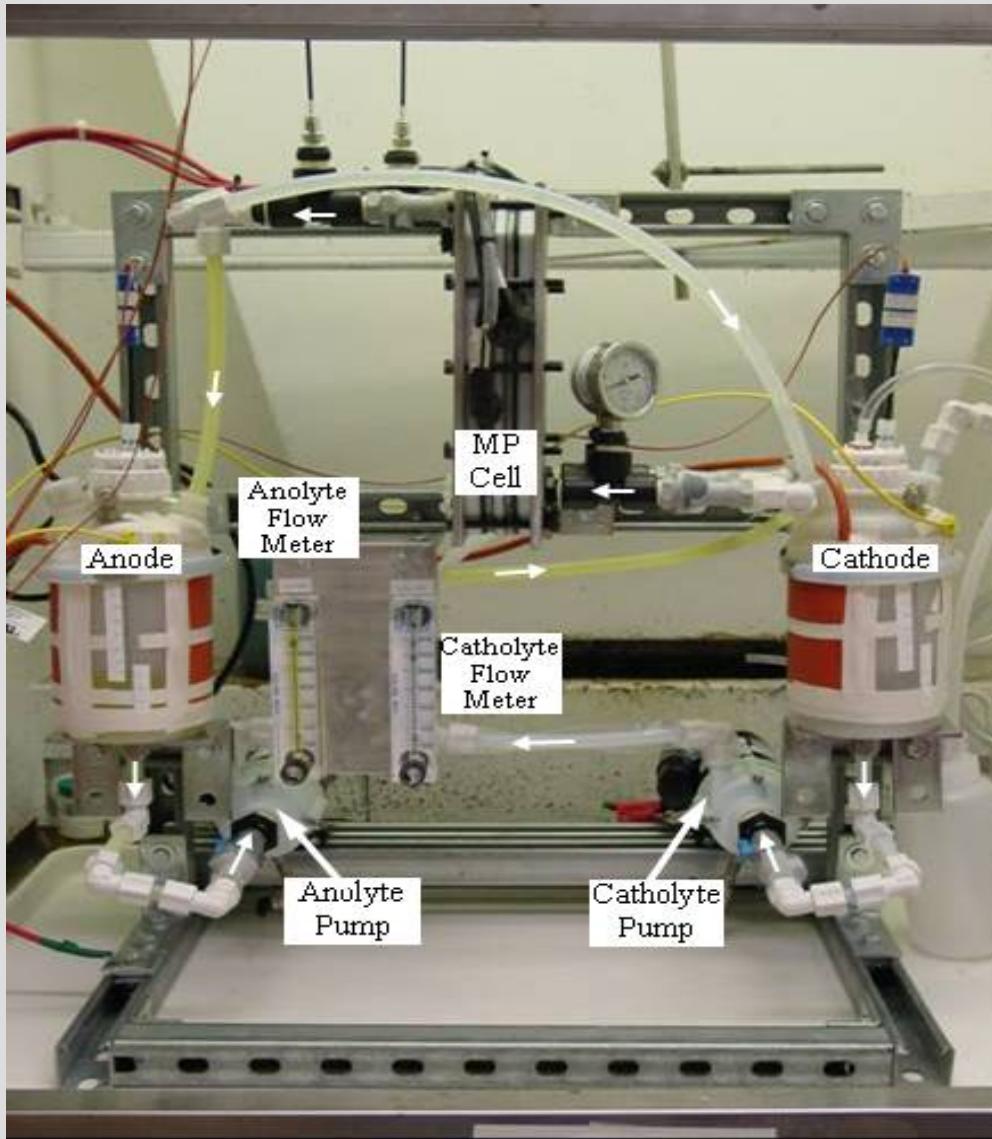
1. Preliminary tests show that higher current densities can be achieved with lifetimes still undetermined.
2. Lower cell voltage has given outstanding lifetime performance
3. Further tests are planned to help establish optimal operating conditions and performance reliability.

NaSICON Development Status

- ▶ Validated technology at lab scale with non-radioactive waste simulant and actual waste
 - ▶ 3500 hours of continuous operations of a cell using simulant AP104 chemistry
 - ▶ Made 50 wt % caustic product from actual radioactive waste
- ▶ Scaled up of ceramic processing and fabrication (subscale unit)
- ▶ Designed a bench scale prototype device
- ▶ Performed preliminary process cost economics
- ▶ Preconceptual design layout prepared
- ▶ Plans to conduct larger scale simulant tests

Radioactive Bench-scale unit installed in fume hood @ RPL

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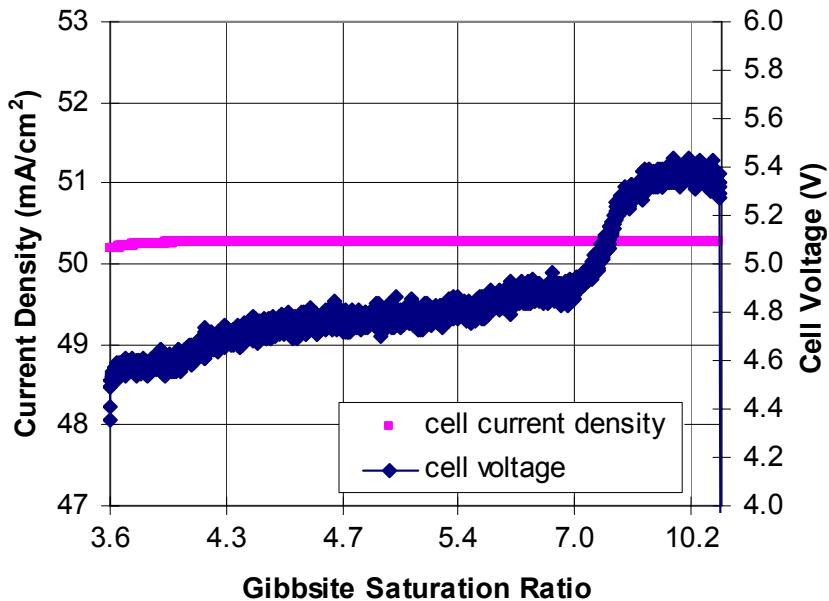


Experimental Conditions

Membrane Type	NASGY (876 GY)
Membrane Thickness	1.4 mm
Membrane Diameter	7.62 cm
Current Density	50 mA/cm ²
Applied Current (Min-Max)	2.24-2.29 amps
Applied Voltage (Min-Max)	4.12-5.44 volts
Temperature	37-43°C
Active Membrane Area	45.6 cm ²
Anolyte Flow Rate	2.4-2.5 L/min
Catholyte Flow Rate	1.9-2.7 L/min
Scaffold Configuration	S3 edge seal with EPDM o-ring
Catholyte	1M & 19M NaOH
ΔP max	≤ 0.25 psig
Operating ΔP	1.6–1.9 psig

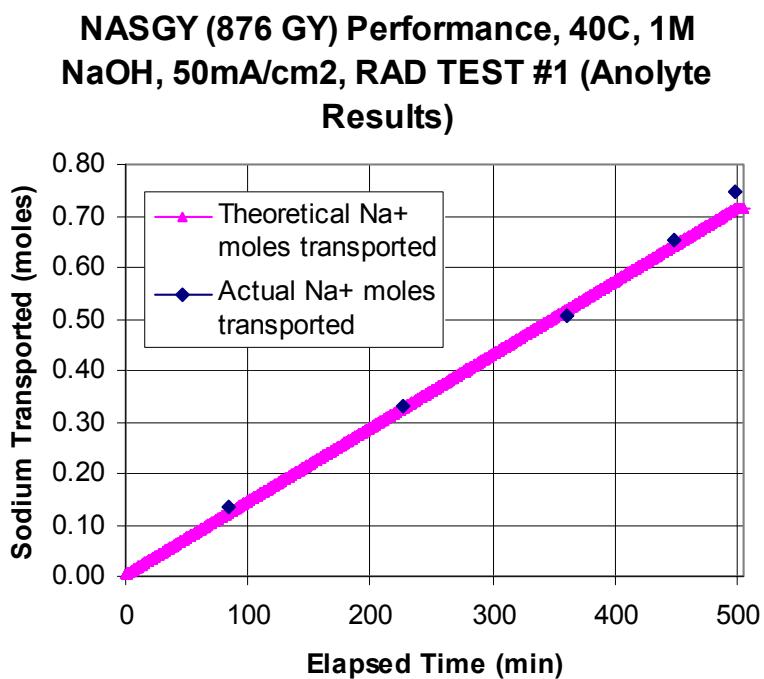
19M NaOH Catholyte Test

NASGY (876 GY) Performance, 40C, ~18.5M NaOH, 50mA/cm², Rad Test #2

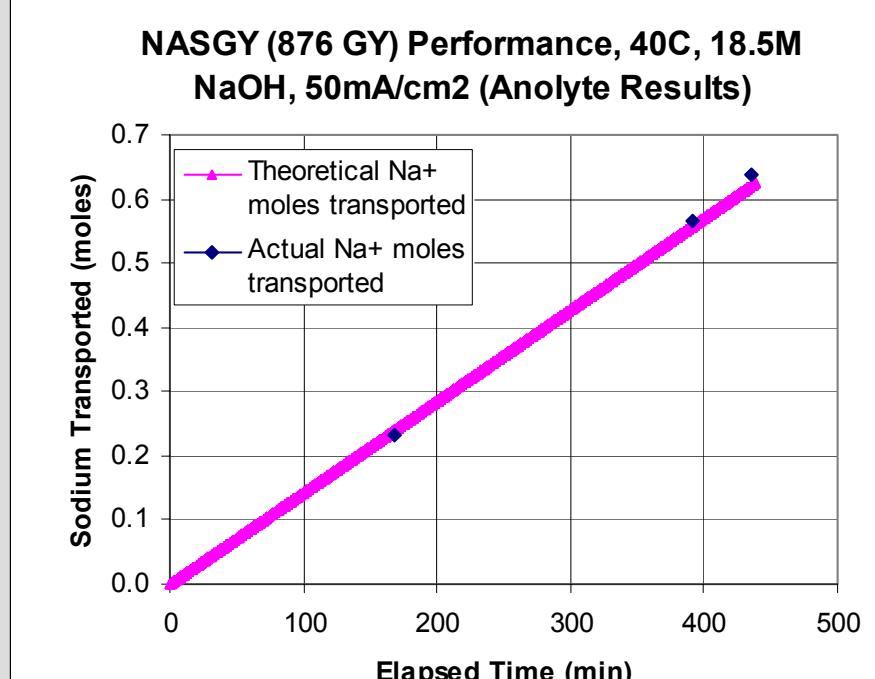


Na Transport Results

Anolyte (1M NaOH)



Anolyte (19M NaOH)



Both sets of results are in good agreement with theoretical Na transport based on applied current (varied 95-103% of theoretical based on anolyte results). Na transport based on OH⁻ titration results.

Radionuclide Transport

	Test 1			Test 2		
	Anolyte Initial (μ Ci/ml)	Catholyte Final (μ Ci/ml)	Df (initial/final)	Anolyte Initial (μ Ci/ml)	Catholyte Final (μ Ci/ml)	Df (initial/final)
Total β	1.75E+00	4.66E-05	37446	6.11E-01	7.04E-05	8679
Sr-90	7.14E-01	<4.0E-5	>17850	2.44E-01	<4.0E-5	>6100
Co-60	1.53E-03	<2E-6	>765	1.48E-03	<2E-6	>740
Sb-125	2.01E-03	<5E-6	>402	1.84E-03	<5E-6	>368
Sn/Sb-126	1.71E-03	<2E-6	>855	1.30E-03	<2E-6	>650
Cs-137	3.00E-02	1.28E-05	2344	3.06E-02	1.85E-05	1654
Eu-154	6.17E-04	<5E-6	>123	1.11E-04	<5E-6	>22
Eu155	2.37E-04	<6E-6	>39.5	3.90E-05	<7E-6	>6
Am-241	7.09E-04	<1E-5	>70.9	9.78E-05	<3E-5	>3

Cs^+ Selectivity = > 2330 (1M NaOH)

Cs^+ Selectivity = > 1640 (19M NaOH)

Al, K, and Sr were not detectable in the catholyte ICP data.

Conclusions from Test Results

- ◆ Average Na separation rates of 10.5 kg/day/m² (1M NaOH) and 10.9 kg/day/m² (19M NaOH)
- ◆ No detectable transport of Al, K, or Sr.
 - ◆ Cs+ Selectivity = > 2330 (1M NaOH)
 - ◆ Cs+ Selectivity = > 1640 (19M NaOH)
- ◆ Initial process voltage change not observed until a gibbsite saturation ratio of ~ 7.7 was reached.
- ◆ No Al precipitation observed in samples obtained at saturation ratios up to 8.9 after 4 months.

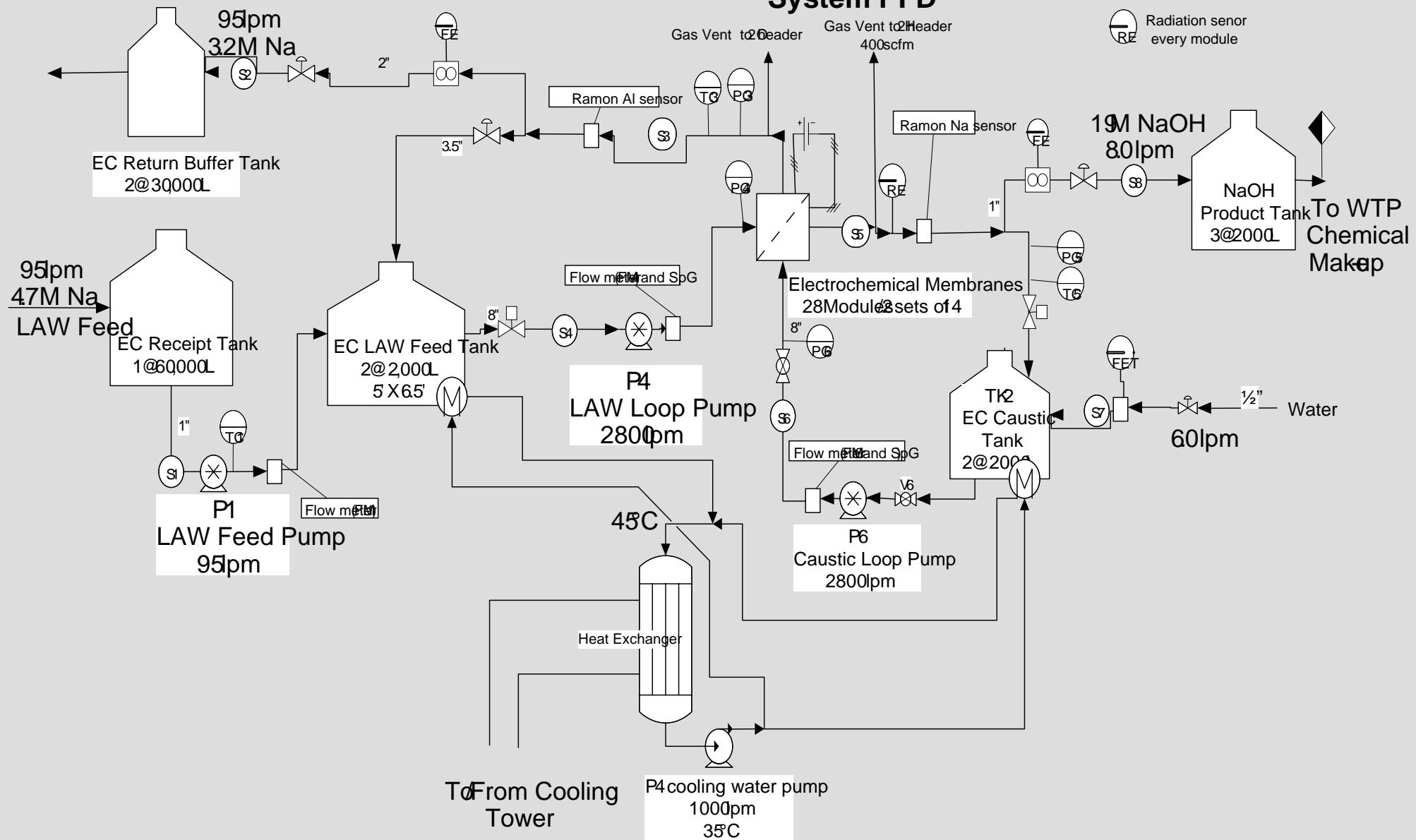
Major Assumptions for Design and Cost Analysis

- ❖ Feed vector: from Tank Farm Contractor Operation and Utilization Plan (TFCOUP) document.
- ❖ Caustic requirement: 15,000 to 36,000 MT of Na as NaOH over 25 years of processing.
- ❖ Caustic recycle operates at ~45°C and 60% online efficiency. (* Current assumption for WTP is 78%)
- ❖ Caustic recovery limited by Al precipitation rate at @ 45°C. Supersaturated LAW will be produced at 25°C.
- ❖ Cesium ion exchanged feed received @ 95 L/min.
- ❖ LAW Waste loading @ 23 wt% Na₂O with cost of \$10K/MT of glass to produce.

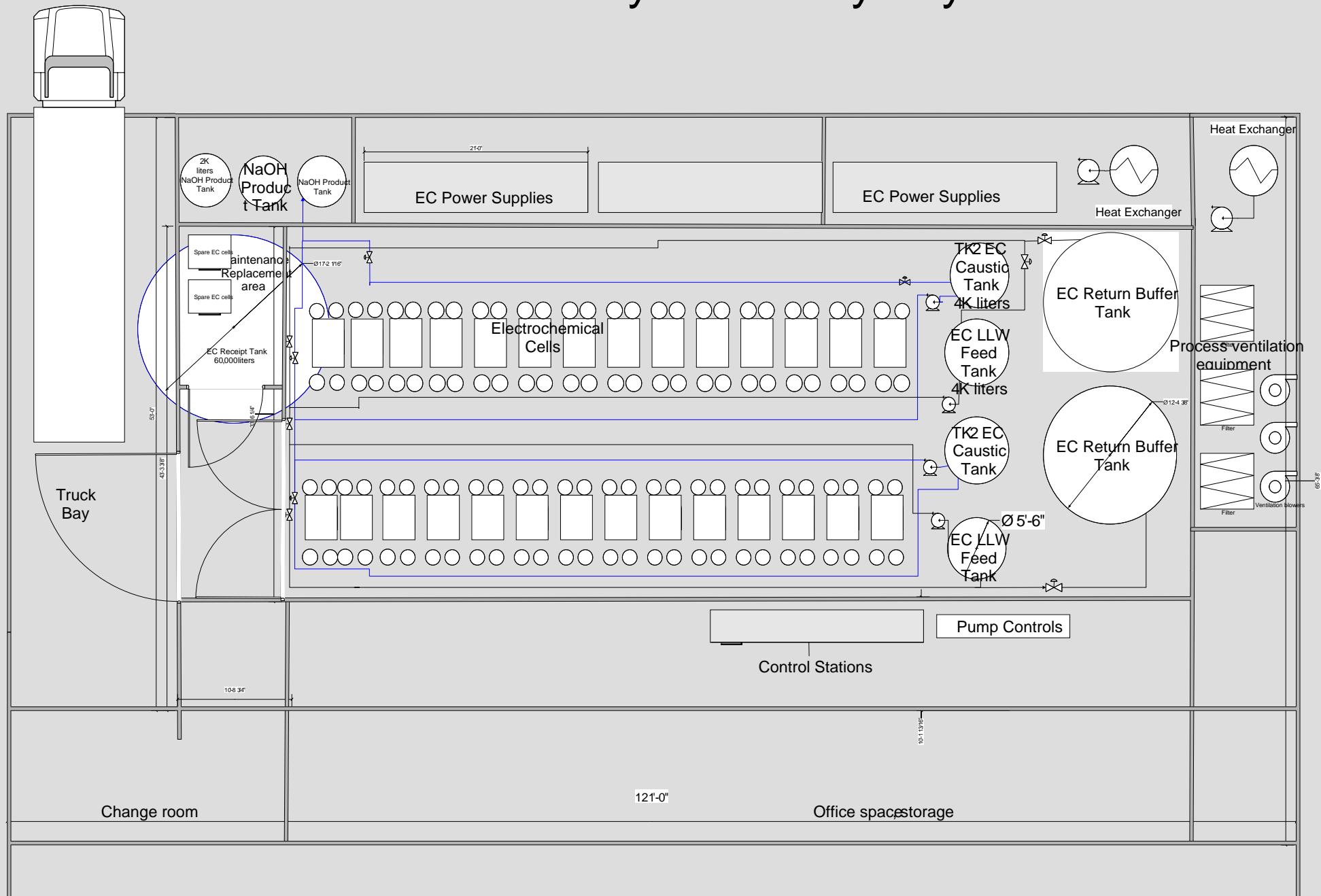
Preconceptual Design for 23,000 MT

- ◆ Power requirements ~2MW
- ◆ Lag Storage Tanks
 - ◆ One 60k liter Receipt Tank, Two 30k liter LAW Return tanks
 - ◆ Two 2K liter feed tank with agitators
 - ◆ Two 2k liter NaOH tanks
- ◆ Vertical Cantilever Recirculation Pumps @ 2800 lpm
- ◆ Cooling water flow of 1000 lpm
- ◆ Twenty eight Prod Modules with 40 cells each
- ◆ Building HEPA filters and ventilation blowers- 80,000 cfm

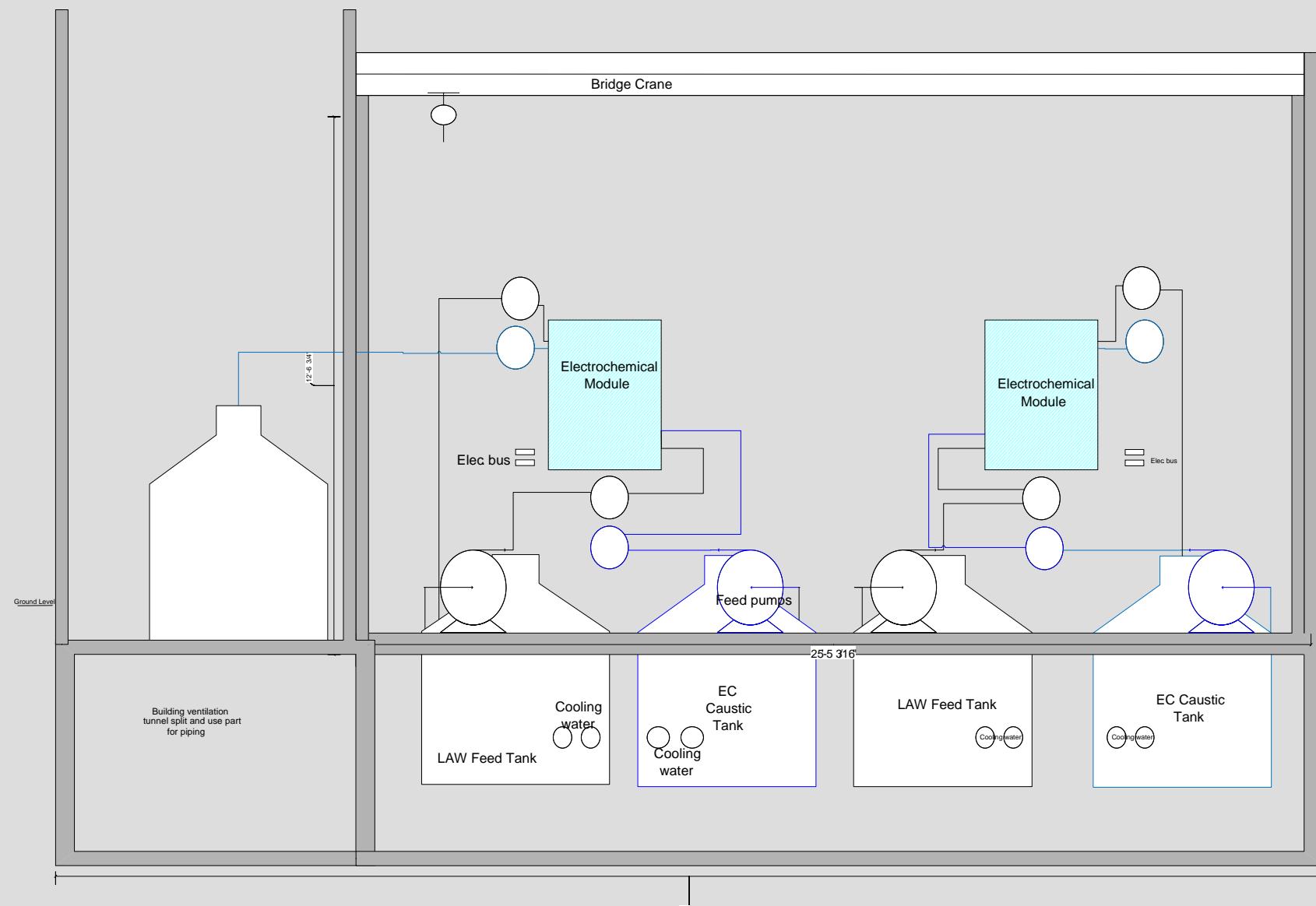
Preliminary Caustic Recycle System PFD



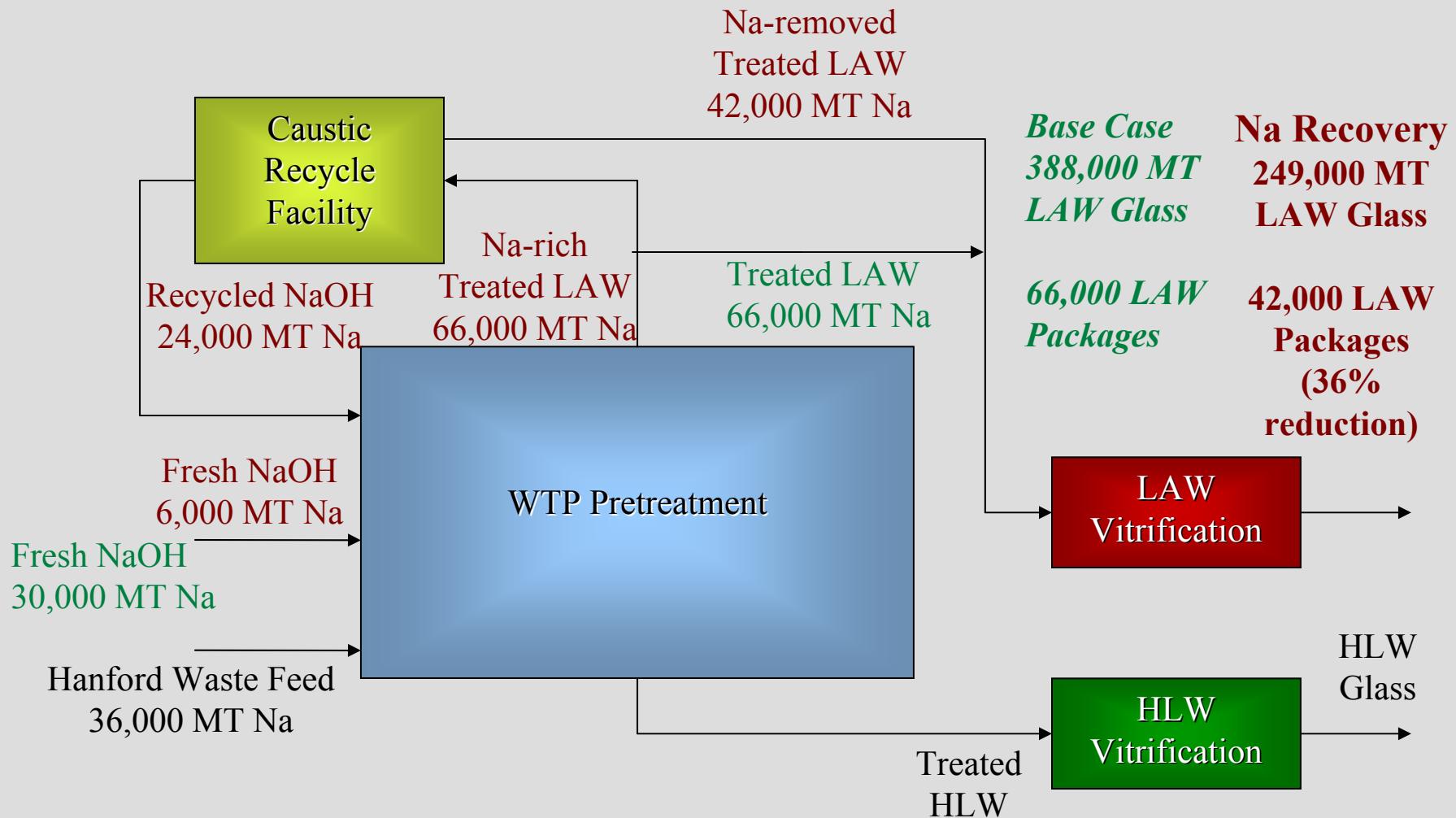
Sodium Recycle Facility Layout



Sodium Recycle Facility Elevation

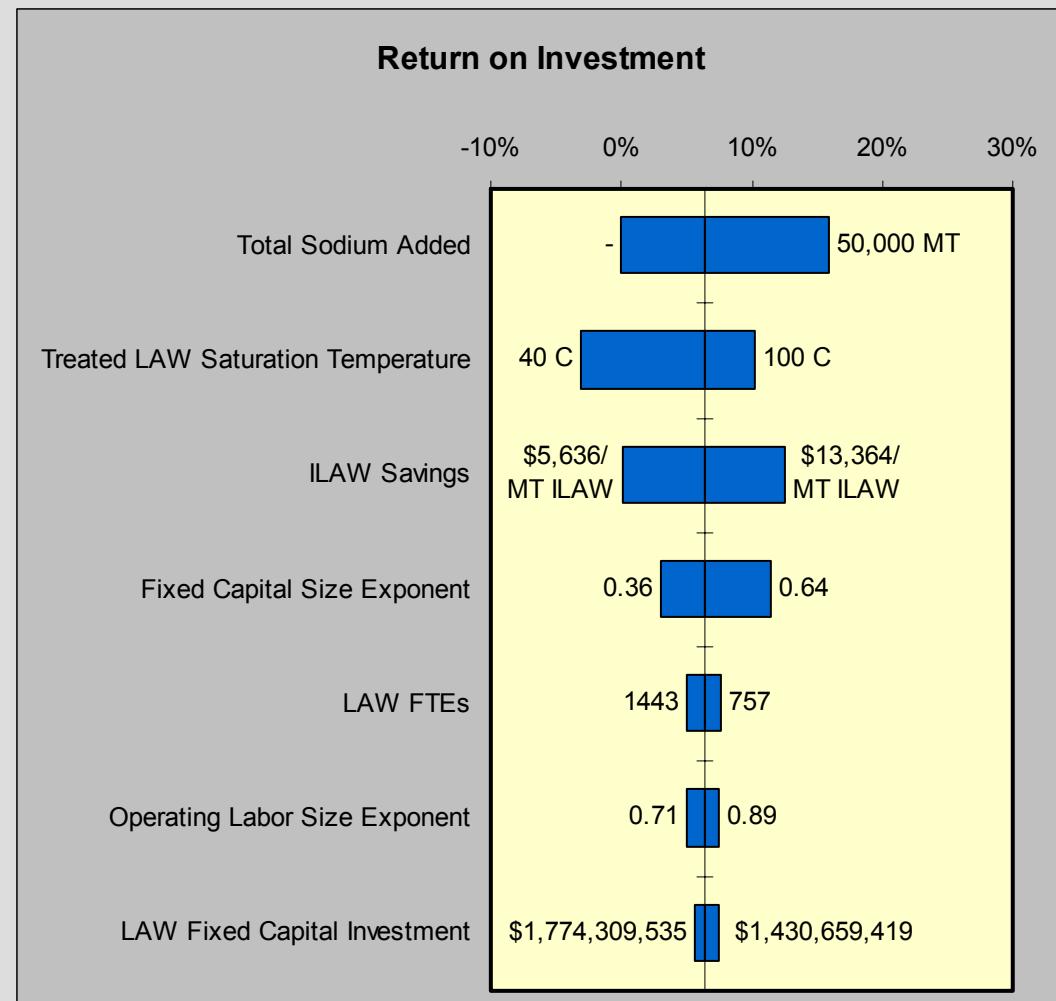


WTP Only- Nominal Case with and without Sodium Recovery and Recycle



Sensitivity Analysis

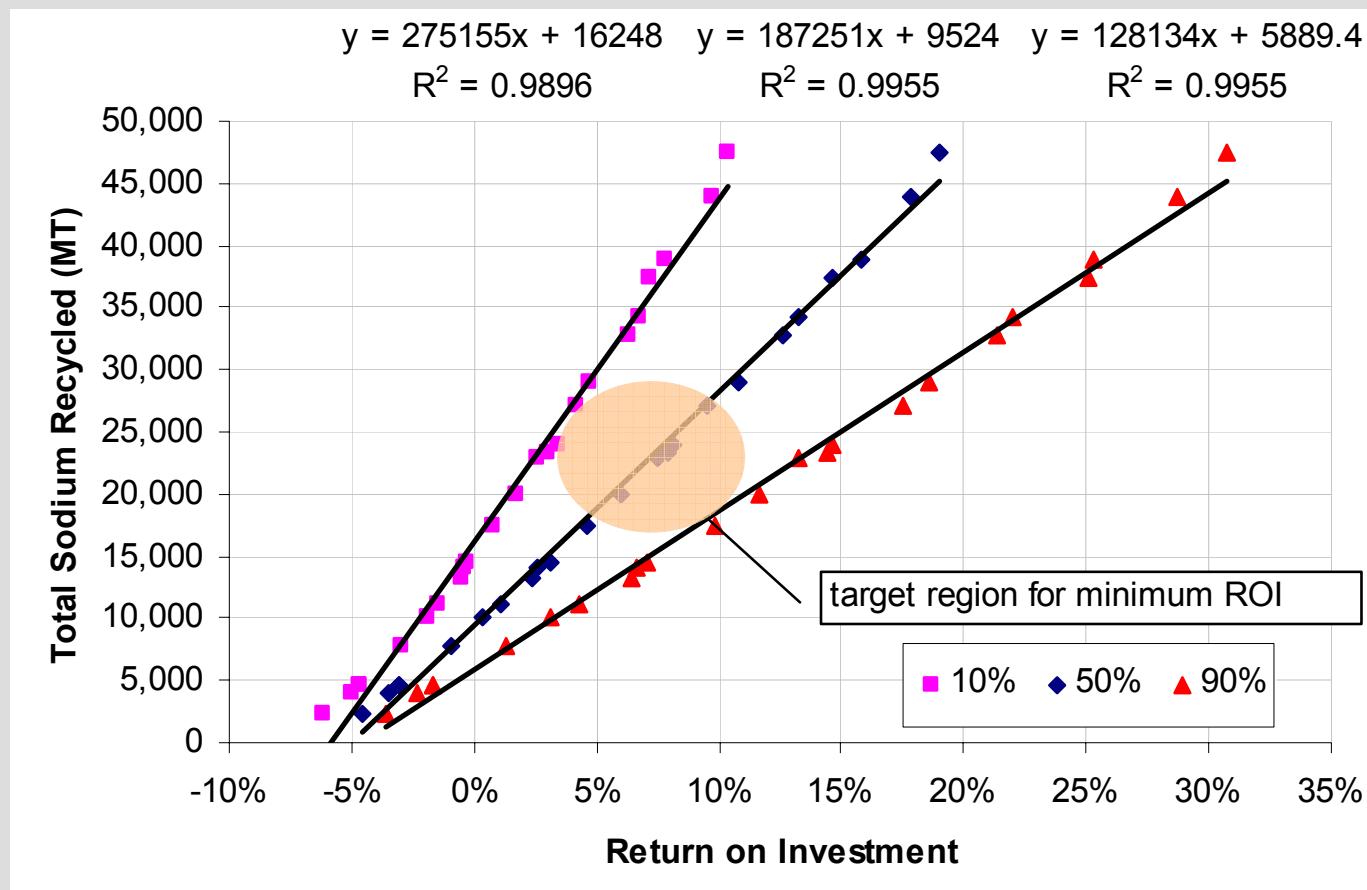
- ❖ Priority of key questions to answer:
 - ❖ How much sodium is added for caustic leaching?
 - ❖ What level of saturation is tolerable?
 - ❖ What is the cost benefit from minimizing ILAW mass?
 - ❖ What are the facility capital and production costs?



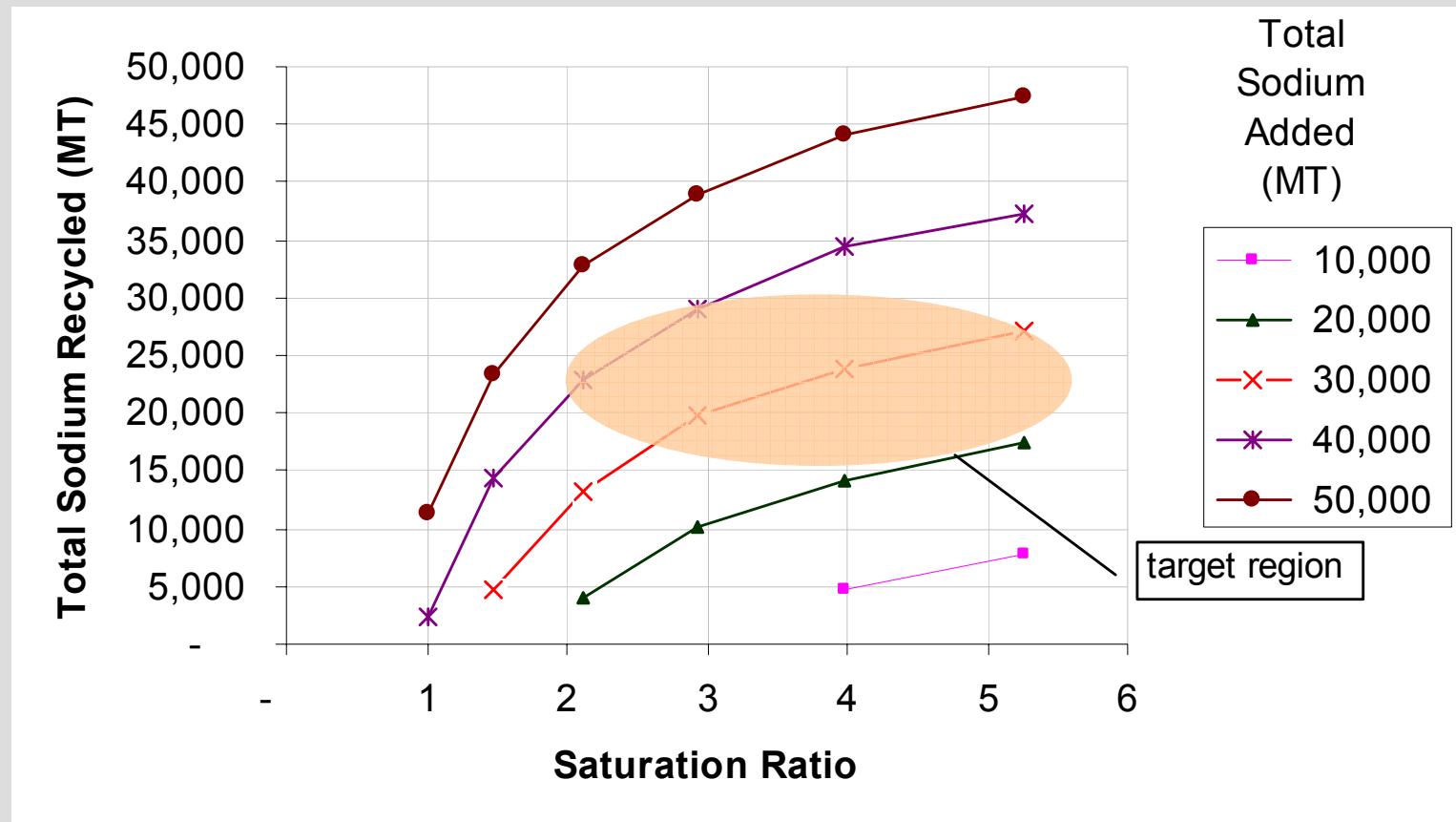
Graph of Return on Investment

Monte Carlo based estimate to provide result band rather than single point estimate

- ◆ Details in Battelle report to be published
- ◆ Capital and labor costs estimated from non-linear scaling equations
- ◆ Cost Benefit range from \$5,000/MT ILAW to \$14,000 MT/ILAW
- ◆ Considers removing sodium to various levels of aluminate solubility in LAW product
- ◆ 10% ROI is equivalent to billions of dollars gross cost savings



Sodium Aluminate Saturation Levels



- ◆ 30,000-40,000 MT Na expected to be added for caustic leaching
 - ◆ 15,000-35,000 MT Na to be recycled over a saturation ratio of 2-5

Summary of Technical/Cost Evaluation

- ❖ Up to 50 % caustic produced from AP104 type simulant.
- ❖ Performance reliability over 4 months of continues operation established with LANS type ceramic structures
- ❖ Validated technology at lab scale actual waste
- ❖ The return on investment is positive and could save between \$100M and \$200M.
- ❖ The cost estimate is most sensitive to amount of Na available for recycle and the allowable saturation ratio of $\text{Al(OH)}_4^- / \text{Al(OH)}_4^-$ (saturation)
- ❖ Life of the ceramic membrane and flux rate is very important in determining facility size and overall costs.
- ❖ Cost for producing immobilized LAW packages important parameter. Cost per MT of LAW glass used in analysis was \$5-14K.